

# A spin-boson theory for charge photogeneration in organic molecules: Role of quantum coherence

Yao Yao

*State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China*  
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The charge photogeneration process in organic molecules is investigated by a quantum heat engine model, in which two molecules are modeled by a two-spin system sandwiched between two bosonic baths at their own temperatures. The two baths represent the photon emission source and the phonon environment, respectively. We utilize the time-dependent density matrix renormalization group algorithm to investigate the ultrafast quantum thermodynamical processes of the model. We find that the transient energy flow through the two spins behaves a two-stage effect: The first stage shows a coherent dynamics which represents the ultrafast delocalization and dissociation of the charge-transfer state, and in the second stage a steady current is establish. The photo-to-charge conversion is highly efficient with the maximum efficiency being 93% with optimized model parameters. The survival entanglement between the two spins is found to be mostly responsible for the hyper efficiency.

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## I. INTRODUCTION

In nature, the charge photogeneration takes place in the light-harvesting systems such as green sulfur bacteria, in which the photon-to-charge conversion efficiency is remarkably high as in the extreme conditions the efficiency could be approximately 100% [1–3]. It is recognized that a long-lived quantum coherence gives rise to the hyper efficiency. The time-resolved two-dimensional optical spectroscopy experiment in Fenna-Matthews-Olson antenna complex revealed that the coherent time is incredibly longer than 400ps [4]. On the contrary, however, the artificial photocells based upon the organic molecules merely produce the efficiency around 10% [5]. The deleterious factors in the molecular materials such as the disorders and the traps break the quantum coherence, leading to significant reduction of the charge carrier's mobility and the conversion efficiency [6]. In this context, people devoted ever-growing efforts in the last two decades to minimize the deleterious process in molecular photocells in order to get higher conversion efficiency. The essential contributions rely on the polymer-based solar cells in terms of the bulk heterojunction (BHJ) structure along with high-conductivity polymers [7]. A long-term interest of the community is then to uncover the intrinsic working mechanism of BHJ photocells.

The process of photogeneration in the BHJ photocells consists of three steps [8]: (i) A donor molecule (polymer) staying at the ground state is excited by the photon energy to form an exciton, which moves and quickly reaches the donor-acceptor interface due to the structure of BHJ. (ii) Through an ultrafast transition process, the electron in the exciton transfers into the neighborhood acceptor molecule (fullerene or its derivative) and forms a charge-transfer (CT) state along with the hole staying in the donor molecule. (iii) The electron further moves away from the hole and becomes a free charge carrier, producing the useful work of the photocell. The CT state

which only exists in the organic photocells is essential for the charge photogeneration. It is the origin of free charges and useful work, but it may at any time geminately recombine and lose the excitation energy to the environment making the useful work and efficiency decrease. As the dielectric constant of organic materials is rather small (about 3 – 5), the mean distance between the electron and hole in the CT state is thought to be short, which induces a relatively large Coulomb attractive energy. Intuitively, it then seems more likely for the CT state to recombine rather than to dissociate to free charges [9]. Hence, the possible ingredient of the driving force for the dissociation of CT state is hotly discussed. The possibilities include the electric field [10], the energy disorder and entropy driving force [11], the excess energy that from exciton to CT state [12], and the charge or exciton delocalization [13].

Recent experimental researches focused on the delocalization of wavefunctions in the polymers and the role of quantum coherence [14–18]. A pump-push technique was utilized, in which the push pulse is to make the CT state repopulate and enhance the population of the relevant hot CT state [14]. Due to the delocalization and the energetics, the hot CT state is easy to be dissociated. This statement was demonstrated by the observations that the decay of the transient photocurrent could be greatly slowed down. Further experiment based on the transient absorption spectroscopy investigated the role of spin in the recombination [15]. It was motivated by the realization that, if the electron and hole in the CT state are bound with each other very tightly the geminate recombination will be dominant, otherwise the bimolecular recombination matters. The spin participates only in the latter case which is essentially observed in the experiment, implying the significant role of the bimolecular recombination and thus the CT state delocalization. A recent experiment further contributed to the role of electric field that is induced by the separation of

the electron and hole [16]. Accordingly, the boundary of the coherent and localized phase was established which is critically important for the study of quantum coherence in organic photocells. In addition, another group also made use of the transient photoinduced absorption measurement to study the BHJ photocells made by various fabrication approaches, and the exciton delocalization mechanism was proposed [17]. Very recently, the coherent ultrafast charge transfer process was comprehensively investigated, indicating the significant role of the vibrational modes [18].

Based upon all these experiments, a physical mechanism of the coherent delocalization comes up. It indicates that, when the CT state is formed the electron and hole rapidly separate due to the coherent expansion of the wavefunctions in polymers. The mean distance between electron and hole becomes much larger than that from the theoretical expectation. Consequently the Coulomb attraction in between is greatly reduced and the dissociation of CT state becomes much more likely. This mechanism then explains the high-efficient performance of BHJ photocells. In this context, we are presently on the stage of the in-depth theoretical study on the delocalization and coherent dynamics in organic photocells.

Theoretically, the coherent dynamics in organic semiconductors has been widely studied in the past. The variational theory was firstly used in the pioneer work of Silbey [19], who studied the coherent and incoherent components of the mobility very carefully. The recent research interest in related subjects emerged in the study of crystalline and semi-crystalline organic materials, motivated by the development of organic field-effect transistors based on the pentacene [20]. In such devices over a certain temperature extent, the mobility is found to decrease with increasing temperature [21], showing the signature of coherent dynamics. In order to make sense of this issue Troisi *et al.* proposed the dynamic disorder model [22], in which the molecules are described by the transport sites on a one-dimensional chain with the inter-site hopping modulated by the lattice vibrations. Following this line, Ciuchi *et al.* studied a similar system from the perspective of the Kubo formula [23, 24]. Geng *et al.* then introduced the effect of high-frequency intramolecular phonon modes into the model [25]. We have also proposed a physical picture of the decoherence effect into the dynamic disorder model, by incorporating a decoherence time  $t_d$  [26] and the quantum phonon modes [27]. Our very recent work tried to incorporate the formalism of Wigner function to investigate the coherent dynamics of exciton dissociation [28].

On the other hand, an alternative way to simulate the charge photogeneration process borrows the language of thermodynamics, which was firstly suggested by Shockley *et al.* [29]. In the heat engine model they proposed, the photon is emitted by a high-temperature emission source (*e.g.*, the sun), and the environment in which the photocell is immersed behaves as the low-temperature sink. The photon-to-charge conversion is then equivalent

to the process that the photocell absorbs energy from the emission source and does useful work following the loss of heat to the environment. The recombination processes of both exciton and CT state play essential roles in the loss of excitation energy. In order to take the quantum coherence and delocalization into consideration, Dorfman *et al.* employed a quantum heat engine model in which the conversion process is described quantum-mechanically [30]. Taking two molecules into account, the model was adopted to compare the conversion processes in both light-harvesting systems and semiconductors. Another work applied the similar model with delocalized excited states to get more efficient photogeneration [31], and an efficiency of about 40% is subsequently achieved. Furthermore, Wang *et al.* recently utilized the quantum master equations to simulate both the electron and heat current [32]. The model they considered is that based upon the double quantum dots embedding in two leads with the dot representing the donor or acceptor molecule in photocells. The essential physics they concerned is the inter-dot tunneling which dominates the photovoltaic effect to a large degree. Based on their simulations, a significant enhancement of the photovoltaic current is obtained and the optimal value of the tunneling is determined.

In this work, we intend to follow the line of quantum heat engine model to study the ultrafast coherent dynamics and the delocalization in the charge photogeneration within the theoretical framework of spin-boson model (SBM). Similar with the consideration of [32], two molecules (donor and acceptor) are simulated by two spin-halves (two-level systems). The bosonic baths coupled to the two spins represent the emission source and the environment, respectively. The heat to useful work conversion process in the SBM has been extensively studied in the community of thermodynamics [33]. But here we will employ a newly developed method based upon the time-dependent density matrix renormalization group (t-DMRG) algorithm [34] and the unitary equilibration [35]. This method allows us to study the *transient* and *coherent* energy flow through spin systems with merely model-free assumptions. We will investigate the thermodynamics of the model and the photogeneration process wherein. The results will show that a steady energy current, via which we can calculate the conversion efficiency, is quickly established following a stage of ultrafast transient energy flow. In the extreme conditions a hyper conversion efficiency is achieved when the quantum coherence is quenched at the appropriate time. The argument of entanglement will help us to understand the intrinsic physics behind. The paper is organized as follows. The methodology we use is introduced in Sec. II. Calculation results are presented in Sec. III, where the transient energy flow, the conversion efficiency and the evolution of entanglement are discussed. Conclusions are drawn in the final section.

## II. MODEL AND METHODOLOGY

The model we study is motivated by the quantum heat engine model addressed by Wang *et al.* recently [32]. A quantum dot in the model is represented by a spin-half, namely a two electronic level system denoting the ground and excited states of the donor or acceptor molecule, and the inter-dot tunneling between the spins stands for the intermolecular transition at the donor-acceptor interface. The excitons are assumed to emerge in the bulk of the donor and quickly move to the interface to form the CT states, so two bosonic bath consisting of numerous excitons or phonons are coupling to the two spins.

To this end, we employ the SBM [36, 37], with two spins sandwiched in two bosonic baths. The model Hamiltonian reads ( $\hbar \equiv 1$ ),

$$H = J\sigma_1 \cdot \sigma_2 + \sum_{\nu=1,2} \left[ \frac{\Delta}{2} \sigma_{\nu}^x + \sigma_{\nu}^z \sum_i \lambda_{i,\nu} (b_{i,\nu}^{\dagger} + b_{i,\nu}) + \sum_i \omega_{i,\nu} b_{i,\nu}^{\dagger} b_{i,\nu} \right], \quad (1)$$

where  $\sigma_{\nu}$  is the usual notation for Pauli operator of the  $\nu$ -th spin with the superscript  $x(z)$  denoting its respective component on  $x(z)$  orientation,  $J$  the transition constant,  $\Delta$  the tunneling between the spin up ( $|\uparrow\rangle$ ) and down ( $|\downarrow\rangle$ ) along the  $z$  orientation;  $\omega_{i,\nu}$  is the frequency of the boson of  $i$ -th mode coupling with the  $\nu$ -th spin,  $\lambda_{i,\nu}$  the respective coupling constant, and  $b_{i,\nu}^{\dagger}(b_{i,\nu})$  the creation (annihilation) operator of bosons. The frequency of the boson is cut off at  $\omega_c$ , such that the spectral density function is expressed as  $J_{\nu}(\omega) = 2\pi\alpha\omega_c^{1-s}\omega^s$  with  $\alpha$  being the dimensionless spin-boson coupling. For simplicity, we set  $\Delta$ ,  $\alpha$  and  $s$  to be  $\nu$ -independent throughout this work.

In consequence, three terms in the Hamiltonian (1) are mainly concerned. The first term of the right hand side is the transition of the energy between the two molecules, which simulates the charge transfer process from exciton to CT state or vice versa. The constant  $J$ , a similar parameter with the inter-dot tunneling [32], determines the transition rate: A large  $J$  gives rise to the delocalization of the CT state while the small  $J$  refers to the localization. The second term denotes the energy gap  $\Delta$  between the ground state and excited state along  $x$  orientation. With regard to the real case, the energy gap here typically represents the binding energy of the CT state, which is of the order  $\sim 100\text{meV}$ . As we do not intend to consider the effect of electric field, the  $\Delta$  is set to be the same for the two spins. The third term denotes the coupling between the spin and the bath. A diagonal coupling (along  $z$  direction) term is employed which implies the molecule can only be excited by the energy of the left bath and the energy of the molecule can only be extracted by the right bath.

As stated, in the present model the two spins represent the donor and acceptor molecules with the state

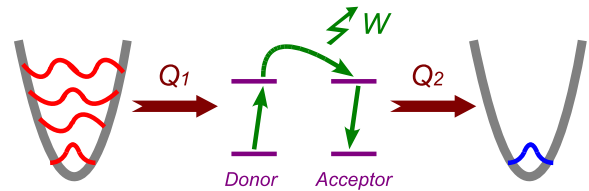


FIG. 1: Schematic for the photocell simulated by two spins coupling with two baths. The two baths are simulated by bosons with different excited energy to denote the respective temperature. The donor is excited by the high-temperature bath, then the excitation energy may transit to the acceptor to form a CT state. The CT state could either lose its energy to the low-temperature bath or store up the energy for useful work. The useful work  $W$  done by the photocell then equals to the difference of the inflow and outflow heat, i.e.  $W = Q_1 - Q_2$ .

$|\rightarrow\rangle(\equiv(|\uparrow\rangle - |\downarrow\rangle)/\sqrt{2})$  being the ground state of the electron and the state  $|\leftarrow\rangle(\equiv(|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2})$  being the excited state [38]. To be specific, as shown in Fig. 1, we denote the first (left) spin as the donor molecule and the second (right) one as the acceptor. They couple to their own bath, respectively. While the device being excited by the photon emission source, the excitons in the bulk of the donor are generated and thus the high-temperature bath is produced. Excitons quickly move to the interface (the two spins in our model) to form CT states and then the useful work is made. Subsequently, an energy current through the spins from the high-temperature bath to the low-temperature one is established. The low-temperature bath accordingly represents the environment taking the recombination of the CT states into account which produces the phonons in the molecules. On the other hand, however, we do not intend to take the respective electron current into consideration. Since the electron current is established much faster than the heat current, it is a reasonable assumption that the electron current does not show any qualitative influence on the heat current [32].

Fig. 1 shows the schematic of the model we study, where the left bosonic bath is at high temperature and the right bath at low temperature. There is an energy current flowing through the two spins with  $Q_1$  being the inflow energy from the left bath and  $Q_2$  being the outflow energy to the right bath. The difference between inflow and outflow energy is that gained by the two spins which will be stored up for the useful work. Thus the useful work done by the photocell could be calculated by  $W = Q_1 - Q_2$ , and the conversion efficiency is

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}. \quad (2)$$

In order to calculate the efficiency it is necessary to properly calculate the inflow and outflow energy. The approaches based upon the master equations are usually used which are convenient to deal with the mixed-state dynamics [32]. Alternatively, in this work, we uti-

lize the pure-state approach on the basis of the t-DMRG and the orthogonal polynomials algorithm [34], via which the time evolution of the SBM with diagonal spin-boson coupling could be investigated with high precision [38]. Based on this method, both the ultrafast charge transfer process and the efficiency with steady state could be computed. Recently, we have studied the unitary equilibration with the algorithm [35], indicating that t-DMRG is very powerful to study the thermodynamics of the relevant models without any model-sensitive assumptions. In particular, with this method it is possible to investigate the coherent and incoherent dynamics in a unified framework, rather than to study the different components separately with the variational theory [19]. Based on these preceding works, we are then able to credibly study the thermodynamics of the quantum heat engine model and the flowing energy wherein.

The calculating procedure is as follows. Initially we calculate the ground state  $|g\rangle$  of the Hamiltonian (1) by the static DMRG method. The light-matter interaction term is then introduced with the form as [39]

$$H_{l-m} = -\hat{\mu} \cdot \mathbf{E} = -\sum_i \vec{\mu}_i (b_{i,\nu}^\dagger + b_{i,\nu}) \cdot \mathbf{E}, \quad (3)$$

where  $\hat{\mu}$  stands for the dipole operator with  $\vec{\mu}_i$  being the transition dipole moment for  $i$ -th mode, and  $\mathbf{E}$  denotes the classical radiation field. The energy of the left bath is substantially enhanced by applying the extern action of  $e^{-iH_{l-m}t_E}$  onto the ground state  $|g\rangle$  with  $t_E$  being the action time of the pulsed field which will be set to  $0.5\pi$ . Obviously,  $\vec{\mu}_i \cdot \mathbf{E}$  are the parameters controlling the energy obtained from the photon emission. Here, in order to guarantee the bath to be stable such that the subsequent results are not sensitive to the microscopic details of the bath, the parameters are set to be  $\omega_c$  for all the modes throughout this work, so that the energy gained by the left bath is at least two order larger than the energy gap of the spins. Afterward, the time evolution of the whole system is calculated by t-DMRG. In the early stage of the evolution the flowing current of the energy will be time-dependent and after an ultrafast process it becomes steady. Accordingly, we target during the time evolution the energy change  $\delta E_L$ ,  $\delta E_S$  and  $\delta E_R$  for the left bath, two spins and the right bath, respectively. Once the steady state is achieved, the energy of the two spins will be approximately unchanged and a steady energy flow is obtained. In this situation,  $\delta E_S/\delta E_L = (\delta E_L - \delta E_R)/\delta E_L$  goes constant which is explicitly equal to the efficiency  $\eta$ , the quantity we want to calculate.

### III. RESULTS AND DISCUSSIONS

In this section, we present the calculating results we obtained for  $\omega_c = 1.0, \Delta = 0.1$ . As we are concerning the delocalization and the quantum coherence of the CT state, in the following calculations we will mainly work in

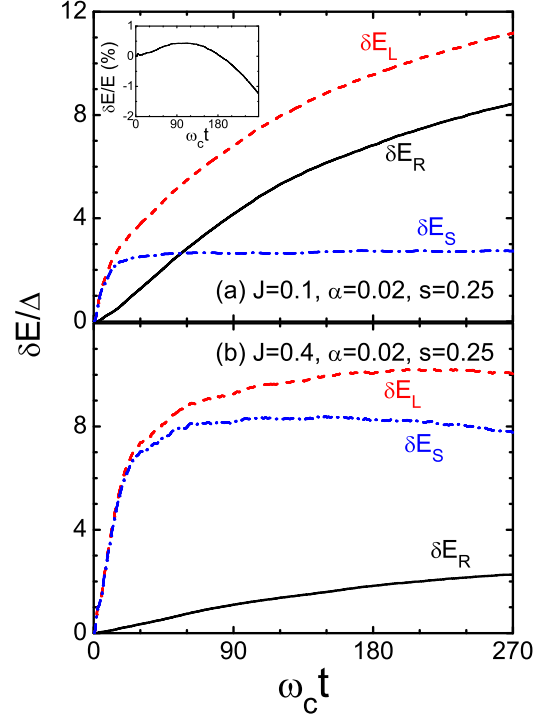


FIG. 2: Time evolution of energy change of the left ( $\delta E_L$ ) and right ( $\delta E_R$ ) bath and the spins ( $\delta E_S$ ). The inset of (a) shows the relative deviation of the total energy during the time evolution. The other parameters are:  $\alpha = 0.02, s = 0.25$ .

the coherent regime, namely the case of the sub-Ohmic spectrum of bath. A number of works have stated that in this regime the spin-bath coupling is relatively strong and the spin dynamics prefers to be coherent and delocalized [40, 41]. We will first show the transient energy flow and based on the steady state we calculate the efficiency in terms of delocalization. The dynamics of entanglement will be shown in the last subsection following with the discussion of the entanglement sudden death. We would like to emphasize here that, to some degree our work motivated to have a proof-to-principle study to apply the quantum heat engine model to the charge photogeneration in organic photocells. Firstly, we do not consider the simultaneous electron current, since we realize it does not significantly affect the heat current due to the incongruous time scale of the two processes. Secondly, we do not intend to explicitly connect the model parameters we set here to that in the practical molecules. However, the reasonable parameter extent for the organic molecules will be kept in mind, such that the subsequent qualitative statement we address is actually useful for the real situation.

#### A. Transient energy flow

We first show in Fig. 2 the time evolution of the energy change of the left and right bath and the spins for

$\alpha = 0.02, s = 0.25$  and two  $J$ 's. It is found that, the energy of the left bath which is initially with high energy changes very quickly right after the time evolution starts. When  $\omega_c t$  is smaller than about 50 the  $\delta E$  of the left bath and the spins are very close, implying the spins gain a majority portion of the energy from the emission source to form the excited state. This is the first stage of the energy flow, and following the time advances the second stage appears. In this stage, the right bath gains almost all the energy emitted by the left bath, while the energy of the spins keeps nearly unchanged during the process. The second stage is closely related to the CT state dissociation which takes place without loss of excess energy. The inset shows the computation error which is measured by the relative deviation of the total energy. It is clearly that the relative deviation is approximately smaller than 1% which is in the reasonable extent.

In order to show the two stages of the energy flow more clearly, we calculate the temporal derivative of  $\delta E_L$  and  $\delta E_R$  which are equivalent to the energy current flowing in and out of the spins. In Fig. 3, the inflow and outflow energy current are shown for  $J = 0.1$  and  $J = 0.4$ . There are clearly two stages: The first stage is  $\omega_c t < 50$  during which the outflow current is much smaller than the inflow current, and the second stage is  $\omega_c t > 50$  during which the inflow and outflow current are nearly the same. In the first stage, we find the energy current of the left bath behaves a relatively regular oscillation, implying the coherent resonance of the emission source and the spins. In the second stage, however, the energy of the spins is saturated and the lineshape of the current becomes chaotic which is a signature of the establishment of the steady energy current.

The two-stage behavior of the transient energy flow is an essential finding of this work. The first stage refers to the coherent interplay between the high-temperature bath and the system, and the second stage shows the incoherent heat flow between the two baths. With respect to the charge photogeneration, the first stage is mainly corresponding to the coherent photon excitation while the second one is to the incoherent recombination. Clearly the ultrafast delocalization/dissociation process of the CT state is closely related to the first stage and the quantum coherence plays a significant role wherein. This conclusion is addressed benefitting from the advantages of our method which takes the quantum coherence into account in a unitary manner. It is worth noting that, in our model there is no channel for the spins to release the gained energy and to make the useful work. The spins can only store up the energy by changing their eigenstates and the respective populations. As we have stated above, a reasonable assumption is that the excited states of the spins are closely similar between the cases with and without the electron current, especially in the presence of the quantum coherence. So the stored energy we calculate here could be directly related to the useful work in the real situations.

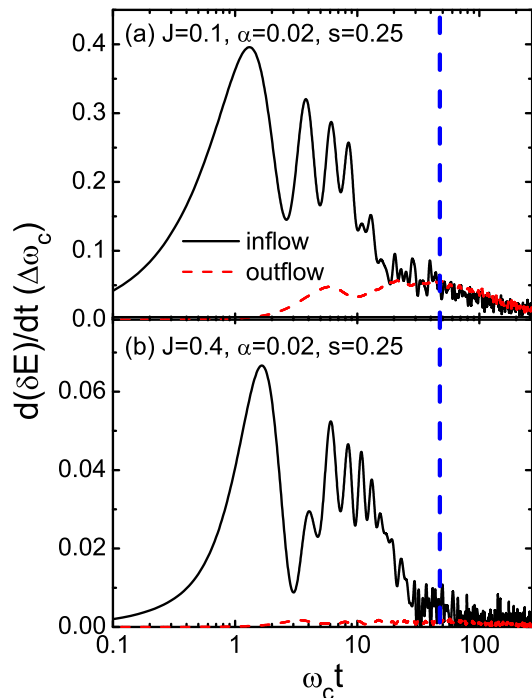


FIG. 3: Time evolution of the inflow and outflow energy measured by the derivative of  $\delta E$  with respect to the time. (a) and (b) refer to  $J = 0.1$  and  $0.4$ , respectively. The blue dashed line shows the division of the two stages of the transient energy flow. The other parameters are:  $\alpha = 0.02, s = 0.25$ .

## B. Efficiency and delocalization

To make a clear connection of our present model and the photogeneration in organic molecules, we show in Fig. 4 the ratio of the energy conversion which measures how much energy from the emission source is transferred to the spins. It is found that, once the steady state is achieved, for the case  $J$  is small ( $J = 0.1$ ) the spins gain a tiny portion (around 20%) of the energy emitted from the left bath, while when  $J$  becomes large ( $J = 0.5$ ), the spins gain the majority (around 85%) of the emitted energy. This effect is easy to understand, since the transition term of Hamiltonian (1) opens a large gap of singlet and triplet states of the two spins depending on the value of  $J$ . When  $J$  is sufficiently large, a single excited electron will carry more energy than that of the small  $J$  case. Thus the excited state in the large  $J$  case could be referred as “hot” state. Subsequently, this effect is due to the delocalization of the spins’ state which simulates the real situation that the delocalized CT state is “hot” with more energy which prefers to dissociate rather than the localized CT state.

In Fig. 5 we show the ratio for another four sets of parameters, that is, to keep  $J$  unchanged and adjust  $\alpha$  and  $s$ . The parameters  $\alpha$  and  $s$  determine the coupling between the system and the bath and the bath’s spectrum, respectively. As stated, in an equilibrated system

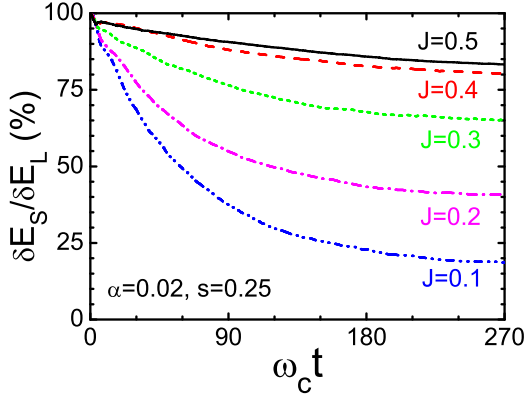


FIG. 4: Time evolution of the energy conversion ratio measured by  $\delta E_S / \delta E_L$  from the left bath to the spins for five  $J$ 's. The other parameters are:  $\alpha = 0.02$ ,  $s = 0.25$ .

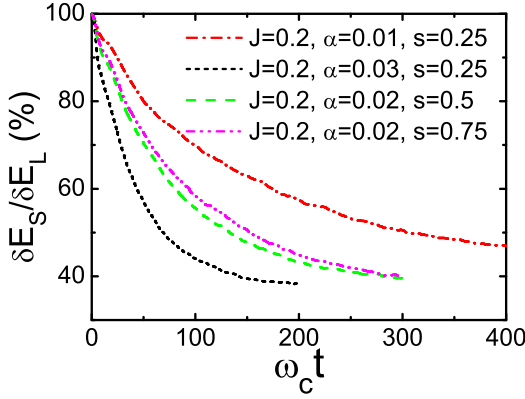


FIG. 5: Time evolution of the energy conversion ratio measured by  $\delta E_S / \delta E_L$  from the left bath to the spins for four sets of parameters.

the physical property is expected to be independent of the microscopic details of the bath's spectrum. Our results prove this statement, as the two curves of the ratio evolution for various  $s$  are almost identical. On the other hand, when we adjust the coupling strength  $\alpha$ , it shows that the steady state is more likely to be obtained for  $\alpha = 0.03$  rather than  $\alpha = 0.01$ . This is easy to understand as the large coupling induces a quick quench of the quantum coherence of the spins. More importantly, for all the three  $\alpha$ 's the conversion ratios seem to decay to the similar value, implying that the efficiency is only weakly dependent of the coupling. The conversion efficiency shown in Fig. 6 supports this result, as we can see  $\eta$  changes a little when  $\alpha$  changes. There is still a small difference which is, as we recognize, due to the limitation of the numerical method. It is also worth noting that, we do not show the long-term evolution for the case of large  $\alpha$  because the numerical precision decays quickly with increasing  $\alpha$  [34].

In Fig. 6 the efficiency of energy conversion is shown which is measured by the steady value of  $\delta E_S / \delta E_L$ . It is clearly that the efficiency increases following increasing  $J$

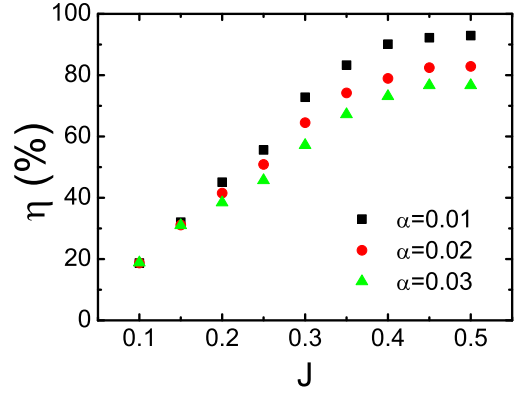


FIG. 6: Efficiency of the energy conversion versus  $J$  for  $s = 0.25$  and three  $\alpha$ 's.

which has been discussed above. The largest efficiency for  $\alpha = 0.01$  is about 93%, far beyond the value obtained by the master equations calculations [31]. This remarkable enhancement of efficiency is mainly originated from the fact that the low-temperature (right) bath is initially at the ground state, i.e. zero temperature. According to the formula of the Carnot efficiency, it should be this large. Meanwhile, the quench of the coherence takes places at the appropriate time benefitting the efficiency enhancement, as from the energy flow shown in Fig. 3 we can find that once the coherence is quenched the energy flow will be greatly reduced. In this situation the energy storied in the spins is not easy to flow out. While in the treatment of the master equations, there is always an available incoherent channel for the outflow energy current to suppress the conversion efficiency. This explains the enhancement of efficiency in the present work compared with the previous one with the quantum heat engine model. In addition, we find that the efficiency undergoes a saturation with increasing  $J$ . This is because the energy gap induced by  $J$  is much larger than the cutoff frequency of the bosons.

As to the real situation, it is evident in the light-harvesting systems that the efficiency reaches to 100%, as we have addressed above. Hence, our result seems more closely to the light-harvesting case. On the contrary, however, in the organic photocells an incoherent loss of excitation energy is quite possible with respect to the nongeminate recombination of charge carriers. So the efficiency in these systems is much smaller than that of the theoretical expectation. In order to improve the efficiency wherein, it is thus necessary to optimize the molecular and device structure to appropriately handle the quantum coherence. As suggested in [32], with sufficient optimization the theoretical limit of efficiency we obtain here is reachable.



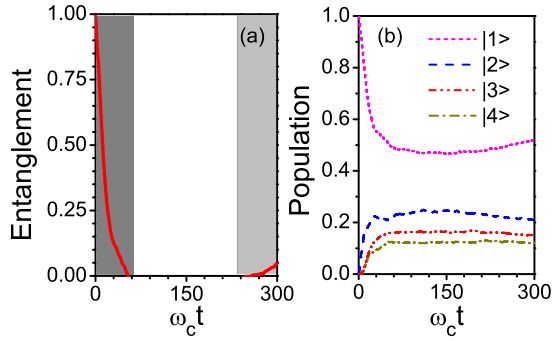


FIG. 7: (a) Time evolution of the entanglement between the two spins. The dark and light areas show the regimes of the entanglement sudden death and revival. (b) Time evolution of the population for the four eigenstates of the two-spins' reduced density matrix. The state  $|n = 1, 2, 3, 4\rangle$  is labeled by the descending order of the population. The parameters are:  $J = 0.4, \alpha = 0.02, s = 0.25$ .

### C. Role of entanglement

The entanglement of the two spins is a useful measurement of the quantum coherence and delocalization. In the presence of the system-bath coupling, the entanglement of the spins would be easy to be quenched by the two baths. It is apparent that the longer the entanglement survives, the stronger the delocalization effect is. Furthermore, we expect that the survival of the entanglement should be consistent with the transition of the two stages of the transient energy flow.

In this work, the entanglement is measured by the concurrence [42]. Fig. 7(a) shows the time dependence of the quantum entanglement between the two spins for  $J = 0.4, \alpha = 0.02, s = 0.25$ . It is shown that there appears an entanglement sudden death (ESD) effect at around  $\omega_c t = 50$ . The effect is synchronous with the transition of the two stages of energy flow, so that it proves our statement above. This two-stage transition can also be seen in the population evolution of the four eigen-states of the spins' reduced density matrix, which is shown in Fig. 7(b). Initially, the spins are residing in their ground state, and following the time advances the population will be quickly transited to the other three states. This transition occurs very quickly and after that the populations keep nearly unchanged during the long-term evolution. In addition, there is a revival of the entanglement after about  $\omega_c t = 240$ . This is also observed in the zero-temperature dynamics [34], which should be related to the robust non-Markovian feature of the bath. Consequently, we would like to address the statement that, the enhancement of the conversion efficiency is strongly dependent of the quench of the non-Markovian entanglement in the process of photogeneration.

As discussed above, the ESD effect we observe here is essential for the charge photogeneration process, since

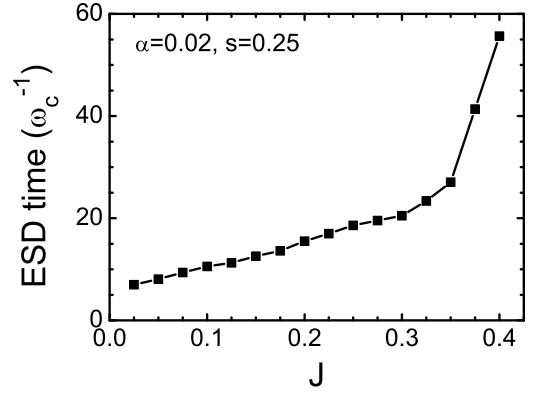


FIG. 8: The time point of entanglement sudden death versus  $J$  for  $\alpha = 0.02, s = 0.25$ .

it is a criterion for dividing the coherent (ultrafast) and incoherent dynamics. Hence, it is useful for us to plot the time point of the ESD in terms of  $J$ , which is shown in Fig. 8. We can find that when  $J < 0.35$  for  $\alpha = 0.02$ , the time of ESD increases linearly with increasing  $J$ . For larger  $J$ , the time of ESD diverges very quickly, and when  $J > 0.4$  the entanglement can not be quenched at all. The point of division here is very similar with the point for the saturation of the  $\eta$  as shown in Fig. 6. This means the survival of the quantum coherence plays an essential role in the conversion efficiency. Thus, the ESD time we compute here is a useful criterion for the estimate of delocalization and photogeneration rate in the real molecules.

## IV. CONCLUSION

In summary, we have made use of the sub-Ohmic spin-boson model to simulate the charge photogeneration process in organic molecules. The two spins denote the donor and acceptor molecules and the two baths represent the emission source and the environment, respectively. The transition constant  $J$  between the two spins refers to the degree of delocalization which is very important for the photogeneration. In our calculations, a two-stage transition of the energy flow is obtained. The first stage refers to an ultrafast energy transition process from the emission source to the spins. Following that, in the second stage a steady energy flow from source to environment is achieved in a completely unitary manner. This effect should be contributive to the research field of the heat current through a spin system. On the other hand, our result shows that the conversion efficiency is strongly dependent of  $J$ , the delocalization, and insensitive to the system-bath coupling and the bath's spectrum. The evolution of the entanglement between the two spins shows its sudden death at short time duration and long-termly revival. The sudden death of the entanglement is synchronous with the transition of the two stages of the transient energy flow, implying the essential role of the

quantum coherence in the transition. Finally, the time point of the sudden death is recognized to be a helpful quantity for the study of the photogeneration.

Two important concluding remarks are worth making. Firstly, the transition constant  $J$  denoting the effect of delocalization is the most important parameter in our present model. If the binding energy of the CT state is 100meV related to  $\Delta = 0.1$ , the chosen value of  $J$  in this work is equivalent to about several hundred meV. This quantity is available in the organic small molecules with good crystallinity or the polymers with long conjugated length. In these materials the delocalization can not be neglected, and our results give the limit of the energy conversion efficiency taking the quantum coherence into

account. Secondly, our results show the bath's spectrum does not affect the photogeneration efficiency. This is theoretically predictable and suggests that in experiment the specific absorption spectrum of the materials does not matter in the charge photogeneration.

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